TECHNICAL MEMORANDUM

MOBILE TAGA SURVEY
GASEOUS PCB's
ONTARIO HYDRO
PCB DESTRUCTION TESTS
FEBRUARY 17 and 18, 1986

ARB-94-86-AQM

August, 1986

Ministry of the Environment
Ontario

C. E. DUNCAN, Acting Director
Air Resources Branch

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Prepared for
The Air Resources Branch
Ontario Ministry of the Environment

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August, 1986

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EXECUTIVE SUMMARY

On February 17 and 18, 1986, the mobile TAGA unit conducted an air monitoring survey at Ontario Hydro's research facility in Etobicoke, Ontario. The survey objective was to provide on-site measurements of ambient PCB's during the testing of a mobile PCB destruction unit operated by Ontario Hydro.

In all, 23 half-hour air samples acquired during the testing period were analysed using the novel TAGA/ASTA technique. At no time were the PCB levels in exceedance of the Ministry guideline of 0.45 ug/m^3. In fact, all of the measurements for ambient PCB's were below the TAGA's detection limits of 0.055 ug/m^3.

INTRODUCTION

As requested by Dr. D. Balsillie, Director of the Air Resources Branch, Ontario Ministry of the Environment, the mobile TAGA unit recently conducted an air monitoring survey at Ontario Hydro's research facility in Etobicoke. The purpose of the survey was to acquire, on-site, measurements of ambient PCB concentrations during the testing of a mobile PCB destruction unit (Class 2) operated by Ontario Hydro. A total of three destruction tests were conducted: two on February 17, 1986 and a third one was completed on February 18, 1986. The TAGA monitored the ambient air for selected gaseous PCBs during all three tests. Mr. Gord Donnelly of the Ministry's Environmental Approval Section provided the TAGA operators with all pertinent information regarding the status of the tests. Throughout the survey the TAGA scientists related the monitoring results to Mr. Donnelly and Mr. Al Jones of the Central Region. This report summarizes the analytical protocol and the results obtained by the mobile TAGA unit.

TAGA TECHNOLOGY AND PCB MONITORING

Basically, the TAGA (model 3000) is a single quadrupole mass spectrometer coupled to an atmospheric-pressure chemical ionization (APCI) ion source. The PCB monitoring technique was originally developed by Sciex Inc. during the late 1970s and it has fundamentally remained unchanged. In recent years the functions of sample collection, analysis and interpretation of data have become increasingly computerized, thereby automating the procedures, enhancing the analytical reproducibility, and virtually eliminating potential operator errors.

In the present system the ambient air is sampled continuously into a preconcentration device commercially known as the Automated Short Term Adsorber (ASTA). The ASTA (shown in Figure 1) consists of two sample probes formed by coiling a nichrome wire coated with a gas chromatographic stationary phase, OV-17. The positions, and thus functions of the two probes, are interchangeable between the adsorption or sampling position, and the desorption, or analysis position. Subsequently, while one probe is adsorbing PCB's from the ambient air, the other probe is being desorbed and analyzed for PCB's from a previous air sample. Altering the positions of the two probes permits

continuous screening of ambient air in 2 minute intervals. There is approximately an eight second delay between sampling periods due to the probe cycling time. Thus a "½-hour sample", which is 15 consecutive 2 minute samples, takes 32 minutes.

When sampling for PCB's the probe is placed directly in the ambient gas stream (1.7 l/s) for a period of 2 minutes. The probe is then changed to the desorb position and 12 volts DC (3.25 amperes) are applied to the probe for a period of 40 seconds. This causes the probe temperature to rapidly increase to approximately 300°C, thereby transferring the PCB's from the OV-17 into the gas phase. The carrier gas, which is a mixture of ultra pure zero air and benzene, constantly sweeps the PCB's into the ion source. Upon entering the ion source the PCB's immediately undergo benzene chemical ionization producing molecular PCB ions which are (mass) selectively monitored by the quadrupole mass filter. The software allows for the screening of 4 PCB congeners at 8 masses, 2 isotopes per congener. Normally the dichlorobiphenyl to pentachlorobiphenyl species are monitored. There are two reasons for this: firstly, the TAGA is more sensitive to the lower homologues, and secondly; PCB's with lower molecular weights generally exhibit higher vapour pressure, thus increasing the likelihood of gas phase detection.

Calibration of the system, including sampling probe adsorption efficiencies and TAGA response, is accomplished by continuously injecting known amounts of PCB's (di to pentachlorobiphenyls) directly into the air sampling steam via a heated injection port (300°C) using a gas-tight syringe and motorized syringe drive. The PCB standards are prepared by the dissolution of pure PCB isomers, one per congener, into iso-octane. Repeated injections at 5 different syringe drive settings establishes a calibration curve which is linear (correlation coefficients are usually better than 0.995) over the PCB concentration range of 0.425 to 2.5 ug/m^3 per congener. The relative standard deviations for multiple injections of PCB standards are typicallv better than 10% at the 0.425 ug/m^3 level.

Throughout the survey air samples were spiked periodicallv with 0.425 ug/m^3 per PCB congener to establish the daily sensitivity factors and determine, on-site, the detection limits of the technique. The detection limit (DL) per congener is defined as being 3 times the standard deviation of the background or

upwind signal observed at the PCB masses, divided by the sensitivity factor. Thus, the DL is a function of the TAGA response per unit ug/m^3 and the variation in background signals. Typical detection limits range from 0.01 to 0.05 ug/m^3 per congener, or from 0.05 to 0.20 ug/m^3 for total (di to pentachlorobiphenyls) PCB's, depending on the complexity of the sample matrix.

DATA PROCESSING AND INTERPRETATION

Immediately following a desorption of the probe, the TAGA computer calculates the level of PCB's (or equivalents) per congener, per isotope, from the net signal (sample minus background) and the daily calibration factors. In fact, for each PCB congener group two measurements are made: one for the chlorine 35 isotope (M); and one for the corresponding chlorine 37 isotope (M+2).

At this stage the field scientist interprets the computer reduced data using the following criteria:

1) the desorption peak (integrated signal) must be at least 3 times greater than the probe noise (S/N > 3);
2) the PCB levels for a given isotope pair must be within the overall experimental accuracy of 20%;
3) the calculated isotope ratios must be within 10% of the theoretical isotope ratio for a given congener.

If condition 1) above is not satisfied, the congener concentration will be below the detection limit and a ND is reported. If conditions 2) and 3) are not evident then a chemical interference at one, or both, of the congener mass(es) is assumed to be present, and the lower concentration value of the two isotopes is assigned the upper concentration limit for that particular PCB congener.

The TAGA/ASTA PCB monitoring technique is a specialized application of the TAGA 3000 designed to screen the ambient air for PCB's. It is important to note the following when assessing the data:

1) The technique measures volatile PCB's i.e. PCB's existing in the gas phase. Airborne PCB's in the form of aerosols or absorbed onto particulate matter are not quantitatively trapped by the probes;

However, should a portion of the nonvolatile PCB's be collected by the probes they would be measured as volatile PCB's;

2) PCB levels are determined continuously every 2 minutes;

3) The PCB sampling probes are analyzed for the more volatile congeners (dichlorobiphenyl to pentachlorobiphenyl), so in fact, the technique does not actually measure all possible PCB congeners (mono to octachlorobiphenyl);

4) The detection limits for the TAGA/ASTA towards PCB's depends upon several factors:

   i) the sensitivity, which is a function of the probe adsorption efficiencies and the benzene chemical ionization rates;

   ii) the level of the interferences (absorbed compounds that have the same nominal ionic mass as the targetted PCB's in both upwind and downwind air samples. Interference levels are highly variable depending on the sampling site, the source(s) in the immediate area, and the local meteorological conditions.

In summation, the mobile TAGA/ASTA technique is a rapid screening method for volatile PCB's, providing near real-time detection at the time when PCB's are potentially released into the atmosphere. It is the only method currently available to the Ministry by which the ambient air can be instantaneously scanned for PCB's, providing valuable information, on-site, necessary for assessing the environmental impact of the PCB destruction process.

RESULTS AND DISCUSSION

In all, 345 2-minute air samples were screened for PCB's using the mobile TAGA/ASTA technique. The PCB congeners targetted were: dichlorobiphenyl, trichlorobiphenyl, tetrachlorobiphenyl and pentachlorobiphenyl. Tables 1 to 3 summarize the monitoring results of the three PCB destruction tests conducted on February 17 and 18, 1986. The readings from fifteen (15) consecutive 2-minute samples were averaged to yield the ½-hour concentrations for total PCB's monitored simultaneously by the TAGA. None of the PCB measurements exceeded the Ministry guideline of 0.45 ug/m^3 for an ½-hour sample. In fact, all the PCB measurements acquired throughout the survey were below the analytical detection limits of the TAGA/ASTA technique.

It was found that the PCB detection limits for this particular survey were exceptionally low due to consistently low background levels of the interferences. As seen in Table 4 over the two test days the detection limits for total PCB's monitored averaged 0.055 ug/m^3, almost an order-of-magnitude below the Ministry guideline. Also, the detection limits per PCB congener were no greater than 0.02 ug/m^3.

During all three tests the mobile TAGA was positioned as close as physically possible to the PCB destruction unit. The TAGA was located just east of the unit next to the pump house (see Figure 2). At this location it is believed that the TAGA was within the aerodynamic envelope created by the surrounding physical structures; that is, the pump house, storage tanks and the mobile destruction unit. It should be noted that the meteorological conditions during the test were generally favourable for this monitoring location. As shown by the meteorological data in Appendix A, the wind speeds for a good part of the monitoring periods were quite low, less than 5 km/hr, particularly on February 18, during the third test. Of course, during periods of easterly winds greater than 5 km/hr, as was sometimes recorded during test 1, the monitoring location may be considered upwind. Unfortunately, locating the TAGA west of the test site was not possible, as shown in Figure 2.

It is noteworthy that the mobile destruction unit does not have an elevated stack, just a small vent located on the north side of the unit approximately 3 meters above ground level. Apparently the volume flow rate from this vent, which is the potential source of PCB's, was only 1 m^3/hr, with the bulk of the gas being comprised of nitrogen.

The TAGA monitored the ambient air for PCB's during all stages of the tests; that is, loading of the tanks, degassing of the contaminated oil, sodium injection, water injection and the pump out. The greatest potential PCB release is probably during the filling of tanks and degassing steps. Regardless, PCB's were not detected in the ambient air during any stage of the tests.

TABLE 1

TAGA PCB SURVEY: ONTARIO HYDRO

FEBRUARY 17, 1986

DATA SUMMARY TEST NO. 1

Sample No.	Time Period	Site	Met. Conditions			½ Hr Av (ug/m^3)
			AT	WD	WS	
1-1	08:10-08:42	1	0	E	5-20	ND
1-2	08:48-09:20	1	0	ESE	0-20	ND
1-3	09:20-09:52	1	0	E	0-15	ND
1-4	09:57-10:29	1	0	E	0-10	ND
1-5	10:29-11:01	1	0	E	0-15	ND
1-6	11:05-11:37	1	0	ENE	0-15	ND
1-7	11:37-12:09	1	0	ENE	0-5	ND
1-8	12:41-13:13	1	0	NNE	0-15	ND
1-9	13:13-13:45	1	0	E	0-15	ND
1-10	13:48-14:20	1	-1	NE	0-15	ND
1-11	14:20-14:52	1	-1	NE	0-10	ND
1-12	14:55-15:27	1	-1	NE	0-10	ND
1-13	15:27-15:59	1	-1	NE	0-10	ND

Note 1: ½-hour average - mean of 15 x 2 minute samples: sum of the di, tri, tetra, pentachlorobiphenyls

2: AT = ambient temperature in degrees Celsius; WD = wind direction; WS = wind speed range in km/hr

3: ND = not detected (less than detection limits)

TABLE 2

TAGA PCB SURVEY: ONTARIO HYDRO

FEBRUARY 17, 1986

DATA SUMMARY TEST NO. 2

Sample No.	Time Period	Site	Met. Conditions			½ Hr Av (ug/m^3)
			AT	WD	WS	
2-1	16:03-16:35	1	-1	NE	0-10	ND
2-2	16:35-17:07	1	-1	NE	0-10	ND
2-3	17:10-17:42	1	-1	NE	0-7	ND
2-4	17:42-18:14	1	-1	NE	0-5	ND

Note 1: ½-hour average - mean of 15 x 2 minute samples; sum of the di, tri, tetra, pentachlorobiphenyls

2: AT = ambient temperature in degrees Celsius; WD = wind direction; WS = wind speed range in km/hr

3: ND = not detected (less than detection limits)

TABLE 3

TAGA PCB SURVEY: ONTARIO HYDRO

FEBRUARY 18, 1986

DATA SUMMARY TEST NO. 3

Sample No.	Time Period	Site	Met. Conditions			½ Hr Av (ug/m^3)
			AT	WD	WS	
3-1	10:30-11:02	1	2	SE	0-3	ND
3-2	11:02-11:34	1	2	SE	0-5	ND
3-3	11:40-12:12	1	3	ESE	0-3	ND
3-4	12:12-12:44	1	3	NE	0-5	ND
3-5	12:44-13:16	1	3	SE	0-10	ND
3-6	13:49-14:21	1	3	SSE	0-3	ND

Note 1: ½-hour average - mean of 15 x 2 minute samples; sum of the di, tri, tetra, pentachlorobiphenyls

2: AT = ambient temperature in degrees Celsius; WD = wind direction; WS = wind speed range in km/hr

3: ND = not detected (less than detection limits)

TABLE 4

ONTARIO HYDRO PCB DESTRUCTION TESTS

SENSITIVITY TO GASEOUS PCBS (ON-SITE) TAGA/ASTA TECHNIQUE

	Feb. 17/86 (Tests 1 & 2)		Feb. 18/86 (Test 3)	
	D.L.[1]	Q.L.[2]	D.L.[1]	Q.L.[2]
Dichlorobiphenyl	0.01	0.03	0.02	0.06
Trichlorobiphenyl	0.01	0.03	0.01	0.03
Tetrachlorobiphenyl	0.01	0.03	0.01	0.03
Pentachlorobiphenyl	0.02	0.06	0.02	0.06
Total (2-5)	0.05	0.15	0.06	0.18

Note 1: D.L. = Detection limit: defined as 3x standard deviation of the background (15 samples) divided by the sensitivity per unit ug/m^3.

2: Q.L. = Quantitation limit: defined as 10x standard deviation of the background (15 samples) divided by the sensitivity per unit ug/m^3.

3: Units = ug/m^3

ASTA SCHEMATIC

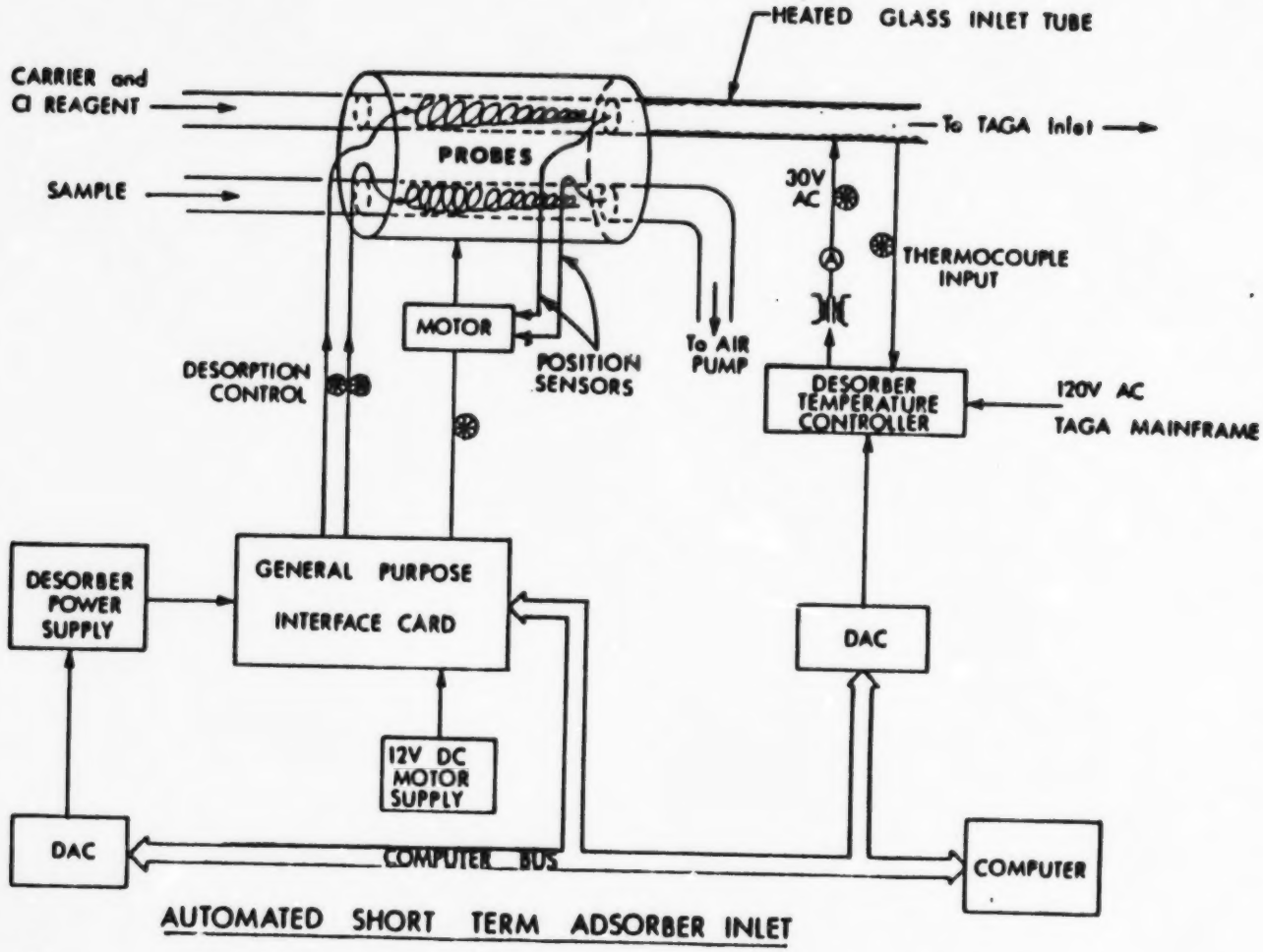


Figure 1: Schematic of the PCB preconcentrator, the ASTA, used in conjunction with the mobile TAGA system for volatile PCBs during the PCB destruction tests.

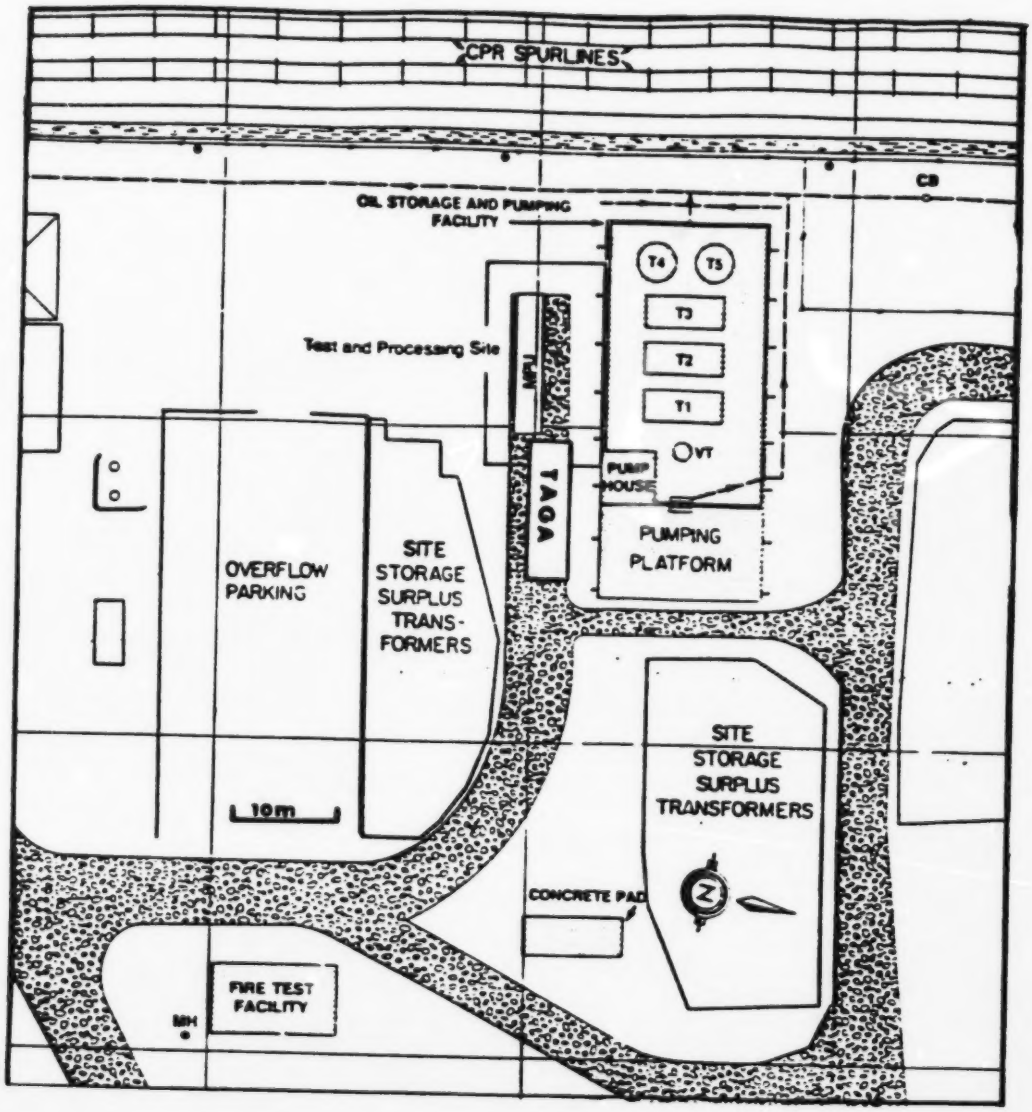


Figure 2: Ontario Hydro's Mobile PCB Destruction Test Site showing TAGA monitoring location for all 3 tests conducted on February 17 and 18, 1986.

APPENDIX A

TAGA PCB SURVEY - ONTARIO HYDRO, ETOBICOKE

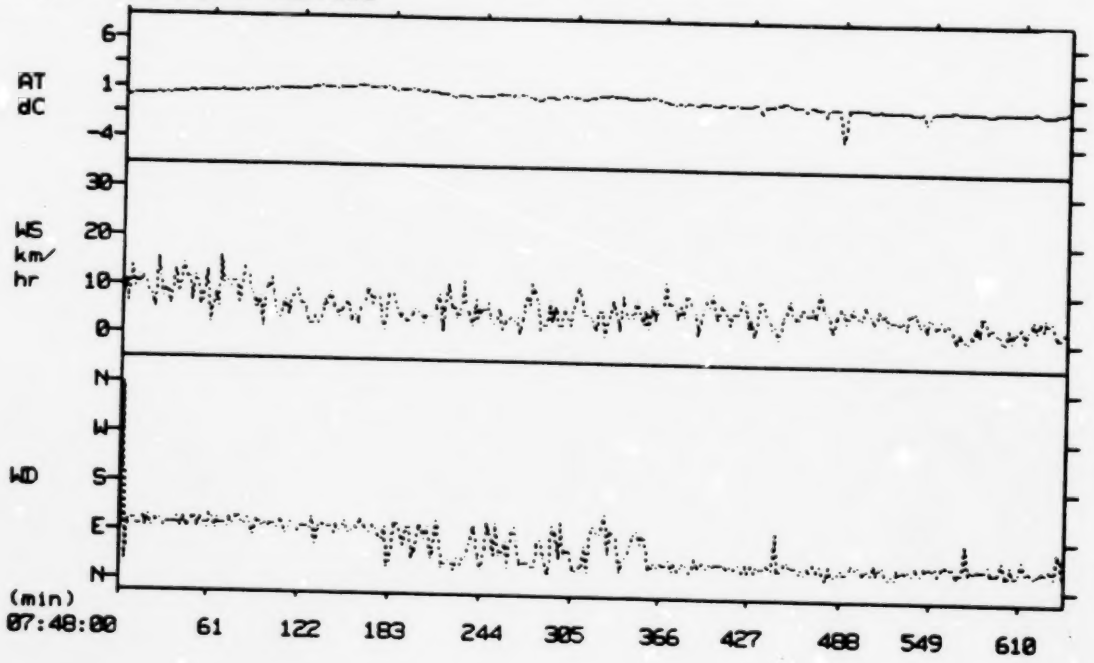
Meteorological Data
Mobile TAGA Station

1. Time scale is expressed as accumulated time (minutes) from the specified start time.

2. Data pertains to all monitoring periods (site 1).

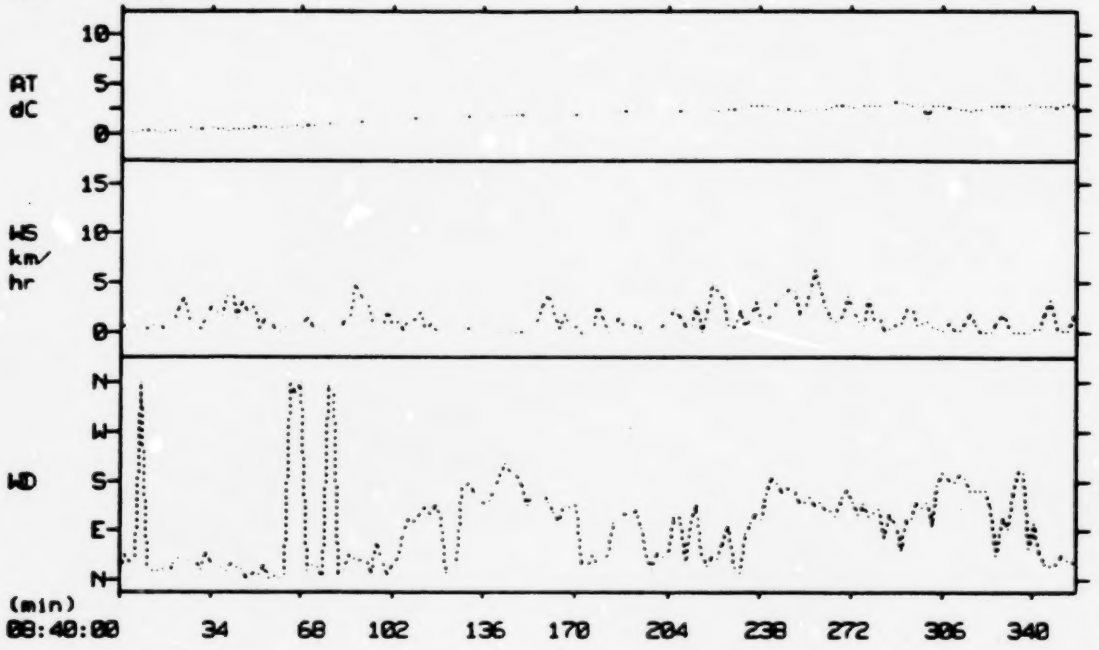
ETOBICOKE:KIPLING

Start: 86/02/17 07:46:00 File: OH1701.MET
Scan : 30 sec Ave: 2.00 min Rep: 2.00 min Rnd: 2.0 min
Loc : INSIDE ONTARIO HYDRO NEXT TO PCB TRAILER
Met : OVERCAST & FLURRIES



ETOBICOKE:KIPLING

Start: 86/02/18 00:30:30 File: OH1801.MET
Scan : 30 sec Ave: 2.00 min Rep: 2.00 min Rnd: 2.0 min
Loc : NEXT TO ONT. HYDRO PCB TRAILER
Met : OVERCAST



(min)
00:40:00 34 68 102 136 170 204 238 272 306 340